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PROPERTIES AND REACTIONS OF LACTIC ACID - A REVIEW

By C. H. Fisher and E. M. Filachione

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PROPERTIES AND REACTIONS OF LACTIC ACID - A REVIEW¹

C. H. Fisher and E. M. Filachione

Lactic acid is an interesting and important chemical (68) for several reasons. In addition to being one of the earliest known organic acids (153, 177) and the simplest hydroxy acid having an asymmetric carbon atom, this acid is important in theoretical chemistry, biological processes, and various industrial fields. Moreover, lactic acid, one of the two simplest hydroxy acids having an alcohol group and structure capable of transformation into an unsaturated acid, is manufactured easily and in high yields from carbohydrates, which in some respects comprise our best and most valuable organic raw materials.

Most of the earlier studies of lactic acid were concerned with physiological phenomena or with stereochemistry and related fields. Many of the recent studies reflect a growing interest in the synthetic and industrial aspects of lactic acid chemistry and the transformation of abundant carbohydrates--through lactic acid as an intermediate--into various industrially valuable products (68), including chemical intermediates, solvents, plasticizers, resins, and elastomers. The present paper deals primarily with the more recent studies.

History

Scheele discovered lactic acid in sour milk in 1780 (153). In 1847, Liebig demonstrated that the sarcolactic acid found by Berzelius (1808) in the fluids of the muscles was different from the lactic acid produced by fermentation. Wurtz in 1858 described the formation of fermentation lactic acid from α -propylene glycol and air in the presence of platinum black; he considered it a dibasic acid. Kolbe contained "lactyl chloride" by the action of phosphorus pentachloride on calcium lactate in 1859. This material was chloropropionyl chloride, and its formation from hydroxypropionic acid was readily explainable. Later (1860) Wurtz called lactic acid a diatomic, monobasic acid, meaning that one of its two typical hydrogen atoms is more basic than the other. Kekule, however, stated that it was simultaneously an acid and an alcohol. Strecker was the first to synthesize lactic acid from alanine, which he had prepared by the interaction of hydrocyanic acid and aldehyde ammonia (153).

The early work aimed at identifying and characterizing the different lactic acids (d-, l-, and dl-forms) was handicapped by their unfavorable physical properties. Being extremely soluble in both water and water-miscible organic solvents and insoluble in other organic solvents, the acids were obtained only with considerable difficulty as low-melting, hygroscopic, and

¹MUCH OF THE MATERIAL IN THIS PAPER WAS INCLUDED IN A TALK GIVEN BY ONE OF THE AUTHORS (C. H. FISHER) BEFORE THE PHILADELPHIA ORGANIC CHEMISTS CLUB ON APRIL 24, 1947.

generally ill-defined solids. In a series of researches initiated in Zurich in 1863, Wislicenus applied both synthetic and degradative methods to the problem of determining the structure of lactic acid (58). In 1873 he obtained unequivocal evidence that the two natural acids have the same structure, that is, that of α -hydroxypropionic acid. His conclusion in 1873 was : "If molecules can be structurally identical and yet possess dissimilar properties, this can be explained only on the ground that the difference is due to a different arrangement of the atoms in space."

After the work of Wislicenus, the optically active forms of lactic acid and many of its derivatives were prepared in pure condition and subjected to intensive study. These investigations and related studies of the transformation of lactic acid into other optically active compounds were important in developing the chemistry of lactic acid and stereochemistry (13, 38, 70, 74, 75, 103, 108, 117, 118, 119, 142, 167, 183).

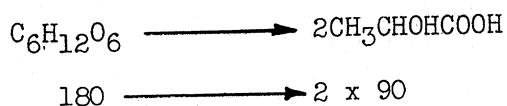
Discoveries in the chemistry of lactic acid were followed by commercial manufacture and use of this readily prepared material. The manufacture and chief uses for lactic acid were developed by Americans, the industry was well established in the United States before the manufacture of lactic acid was undertaken in foreign countries. The first lactic acid factory was established in Littleton, Massachusetts, in 1881 by Charles E. Avery (121, 160).

Manufacture

Although various methods of preparing lactic acid synthetically have been described (47, 52, 92, 138), lactic acid is manufactured in the United States by fermentation of molasses, starch hydrolyzates or whey. The fermentation process (12, 122, 139, 141, 168, 176, 178, 179), as described by Peckham (135), is given below:

Any of several strains of *Lactobacillus* can be used for the fermentation, and some of the molds are adaptable. The procedure in general consists in the fermentation of a carbohydrate together with suitable mineral and proteinaceous nutrients and an excess of calcium carbonate. It is generally preferred to use thermophilic bacteria of the *delbruckii* type, which exhibit their optimum activity at 50°C. Such a fermentation eliminates most contamination problems and permits the use of a growing medium which has been pasteurized, as opposed to the sterilized growing media usually required for mesophilic fermentation. The limit of the concentration achievable by this procedure is the solubility of the resulting calcium lactate at the temperature of the fermentation, approximately 15 percent. The lactic acid as formed reacts with the free calcium carbonate, producing calcium lactate and carbon dioxide gas. This prevents the pH in the fermentation from becoming low enough to inhibit bacterial action.

The theoretical yield of lactic acid is 100 percent of the weight of fermentable hexose sugar according to the over-all equation



In actual practice, this yield is never obtained. It is presumed that a portion of the carbohydrate is utilized by the organism in its metabolism, so that fermentation yields of 94 to 96 percent are normal. Further losses occur during subsequent processing, resulting in a final yield still lower than this figure. The actual loss varies from plant to plant and depends on the type of operation, the equipment selected for processing, and the efficiency of the process. In typical plant operation, yields of about 85 percent are normal.

The lactic acid is purified by crystallization of its calcium salt, steam distillation of the free acid under relatively high vacuum, oxidation or organic impurities with mild oxidizing agents, extraction of the free acid with isopropyl ether, or through its methyl or ethyl ester (7, 49, 135). Amine lactates, such as triamylammonium lactate, can be extracted readily from dilute aqueous solutions (145, 164).

Production of lactic acid in the United States increased from about 10,000 pounds in 1894 to about 400,000 pounds in 1897, and to more than 1,000,000 pounds (calculated as 100 percent acid) in 1917, when there were six manufacturers (160).

As shown in Table 1, production of lactic acid in the United States has increased greatly during recent years (104, 160, 185, 186, 187).

TABLE 1. PRODUCTION OF LACTIC ACID (100% BASIS) IN THE UNITED STATES^{a, b}

YEAR	TECHNICAL, LBS.	EDIBLE AND MEDICINAL, LBS.	TOTALS, LBS.
1939	1,530,456	1,609,094	3,139,550
1940	1,671,237	1,492,301	3,163,538
1941	2,646,000	2,334,000	4,980,000
1942	2,931,000	3,124,000	6,055,000
1943	3,242,000	4,243,000	7,485,000
1944	4,458,000	4,161,000	8,619,000
1945	3,467,000	4,672,000	8,139,000
1946	2,219,000	3,824,000	6,043,000
1947			6,328,000
1948	2,316,000	2,676,000	4,992,000

^a U. S. Tariff Commission Reports; data for 1947 and 1948 are preliminary.

^b Production of sodium lactate: 324,000 pounds in 1944, 129,000 pounds in 1945, 369,000 pounds in 1946, and 153,000 pounds in 1948.

Corn starch hydrolyzates, molasses, and whey are the raw materials commonly used in the fermentative production of lactic acid. Various other raw materials, including Jerusalem artichokes (5), grapefruit juice, (128, 129), corn cobs (71), sulfite waste liquor (116), potatoes (40, 165), starch by-products (180), have been recommended for this purpose.

Physical Properties and Structure

Having an asymmetric carbon atom, lactic acid is capable of existence as the d-, l-, and dl-forms. The acid made commercially by fermentation is substantially the optically inactive dl-form (135), although d-lactic acid can be made by fermentation under controlled conditions (5, 6).

Until recently, the nomenclature used to designate the isomeric forms was confusing. The acid commonly known as sarcolactic, the form occurring in blood, has a (+) rotation but the l configuration. It is, therefore, correctly designated as l(+) lactic acid and its Enantiomorph as d(-) lactic acid. The salts of the l(+) acid are levorotatory, and the salts of the d(-) acid are dextrorotatory. Because of the low optical rotatory power of the free acid, rotation of the pure acid or its simple salts is not a completely suitable indication of the optical form of the acid, or of the percentage composition of a mixture. The benzimidazole derivatives of lactic acid have greater rotatory power, so that either form of lactic acid or the percentage composition of a mixture can be identified readily through the benzimidazole derivative (50). Both optical isomers occur freely in nature, but the lactic acid produced commercially is usually the racemic mixture.

When aqueous solutions of lactic acid are concentrated (15, 62, 174) by distillation, the removal of water is accompanied by auto-esterification of the hydroxy acid (which produces water) unless the concentration is conducted at relatively low temperatures and in the absence of esterification catalysts. The first esterification product is lactyllactic acid, $(\text{CH}_3\text{CHOHCOOCH}(\text{CH}_3)\text{COOH})$, but lactide and higher linear esters, that is, trimeric, tetrameric and polymeric lactic acid,² are formed as the concentration or dehydration proceeds (15, 62, 174). These several components, including water, occur in various proportions in aqueous lactic acid, the extreme limits being pure water and completely polymerized lactic acid, $(-\text{OCH}(\text{CH}_3)\text{CO})_x$. Figure 1 shows the composition of aqueous lactic acid at equilibrium and at progressive stages of dehydration: these data are taken from Bezzi (15) and Watson (174).

As dilute lactic acid is concentrated, it becomes denser and more viscous. Concentrated lactic acid is sirupy, whereas the condensation polymers are soft or firm solids (62, 175).

²THE PREPARATION OF PROTECTIVE COATINGS FROM POLYLACTIC ACID HAS BEEN DESCRIBED (175).

Although lactic acid is usually obtained as a sirupy liquid, the d-, l-, and dl- forms can be obtained in substantially pure form by distilling lactic acid at low pressures (23, 73, 111) followed by crystallization. Table 2 shows the properties of the isomers.

Table 2. - Properties of Optically Active Lactic Acids^a

	Melting Point, °C.	Water absorbed from air at room temperature	Dissociation con- stant at 25°, pK
d(-) Lactic acid	52.8	0 in 4 hrs.; 2% in 20 hrs.	3.83 ± 0.01
l (+) Lactic acid	52.8	1% in 4 hrs.; 3% in 20 hrs.	3.79 ± 0.01
dl Lactic acid	16.8	3% in 3 hrs.; 10% in 15 hrs.	3.81 ± 0.01

A BORSOOK, HUFFMAN, AND LIU (23)

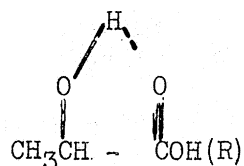
Because of the ease with which lactic acid undergoes auto-esterification when heated, it is difficult to determine the boiling point at most pressures and impossible at atmospheric pressure. Figure 2 gives several boiling points reported for lactic acid; those of hexanoic, octanoic, α -hydroxy-n-butyric, and α -hydroxyisobutyric acids are given for comparison. α -Hydroxyisobutyric acid has a boiling point near that of lactic acid, whereas α -hydroxy-n-butyric acid distills about 15° above the boiling point of lactic acid.

The boiling point of lactic acid calculated by Kinney's method (109) is 191.4°C. Another method, based on the relationship between the boiling points of various acids and their esters (Figure 3), was used to estimate the boiling point of lactic acid. The boiling points of lactic acid estimated from the boiling points of various lactic esters (Figure 3) are: 199°C. (methyl); 194° (ethyl); 190° (propyl); 188° (isobutyl); and 189° (isoamyl). On the basis of these estimated boiling points and Figure 2, it seems clear that lactic acid is moderately volatile and that the difficulty of distilling this acid is attributable to auto-esterification or polymerization. Several investigators have purified lactic acid by distillation (32, 135).

The refractive index of lactic acid as a function of concentration has been reported (155). The heat capacity and heat of fusion of lactic acid have been studied by Huffman and coworkers (99).

Inasmuch as formation of a five-membered ring (shown below) from lactic acid is sterically possible, it might be expected that structures of this type

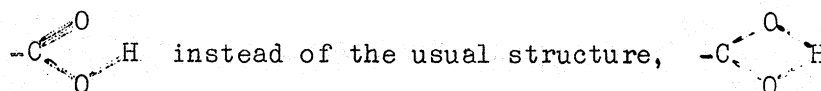
would have transient existence at least and influence the properties of lactic acid. Investigations by several workers suggest that the cyclic structure actually exists.



Bai (11) studied the Raman spectra of lactic acid and its esters and concluded that lactic acid is monomeric. The failure of lactic acid to dimerize in the manner of acetic and other acids can be attributed to the preferential tendency of lactic acid to form a five-membered ring.

Pauling (133, 134) concluded from an infra-red absorption study that ethyl lactate has a structure similar to that shown above and that the hydrogen bridge is weak (1,400 cal. per mole instead of the usual 5,000-8,000 cal. per mole). It was believed that a small proportion of ethyl lactate has a different structure, that is, with the hydrogen directed away from the ester group.

According to Peyches (137), who studied Raman spectra of lactic acid, the carboxyl group has the structure



Since ethyl lactate (and presumably other lactic esters and lactic acid) exists partially in the chelate or cyclic form, it seems likely that intermolecular hydrogen bonding is not so prevalent and important in ethyl lactate as in n-alkanols. This supposition is supported by association calculations (discussed later) and by the boiling points of alkyl lactates and the corresponding acetyl derivatives. Methyl and ethyl lactates boil at 145° and 155° C., respectively, whereas their acetyl derivatives boil at 172° and 182°, respectively. The difference between the boiling points of n-alkanols (comparable in vapor pressure to methyl lactate) and their acetyl derivatives is approximately 13° C. The difference in boiling points of the lactates and their corresponding acetyl lactates is 27°, or twice the usual difference in boiling points of alcohols and their acetates. Probably the 27° difference (instead of 13°) is due to decreased hydrogen bonding between different molecules of the alkyl lactates.

According to data supplied by Bingham and Spooner (16, 17), the intermolecular association of ethyl lactate is considerably less than that of alcohols

and approximately equal to that of acetic anhydride (Table 3). The fact that ethyl lactate--an alcohol-- is less associated than typical alcohols, such as butanol, is in harmony with the claim (133, 134) that ethyl lactate exists largely in the chelate form.

Table 3. - Fluidities and Intermolecular Association^a

Compound	Fluidity, rhes				Association ^a	
	0°	10°	20°	30°	Range	at 200 rhes
Ethyl lactate	18.80	27.17	37.30	48.97	1.49-1.43	1.432
Ethyl propionate	144.1	164.9	187.4	211.4	1.13-1.20	1.182
n-Butyl alcohol	19.0	25.8	33.9	44.4	1.85-1.65	1.732
n-Valeric acid	-	-	44.00	53.1	1.55-1.57	-
Isoamyl alcohol	11.6	16.5	23.2	31.2	1.83-1.54	-
Ethyl hexyl ether	-	-	99	116	1.14	-
Acetic anhydride	80.2	95.2	110.6	126.9	1.30-1.46	1.410

a. Bingham and Spooner (17)

Dissociation constants (51) of lactic acid and certain other acids (Table 4) show that lactic acid ionizes to a greater extent than the simple aliphatic and aromatic acids. This may be attributed (43) to the electron-attracting hydroxyl group on the α -carbon atom.

Table 4. Dissociation Constants of Acids at 25° C.^a

Substance	$K_1 \times 10^5$	Substance	$K_1 \times 10^5$
H ₂ SO ₃	1200	Chloroacetic	137.9
H ₃ PO ₄ ^b	751.6	Glycolic	14.75
H ₃ BO ₃	5.79×10^{-5}	Lactic	13.74
HIO ₃	17300	Cyanoacetic	350
H ₂ CO ₃ ^c	0.0454	Benzoic	6.312
Formic	17.72	Cyanobenzoic	31
Acetic	1.754	o-Chlorobenzoic	122
Propionic	1.336	o-Nitrobenzoic	600
Butyric	1.515	3,5-Dinitrobenzoic	150

a. Dole (51)

b. $K_2 \times 10^{11} = 6226$.

c. $K_2 \times 10^{11} = 5.61$

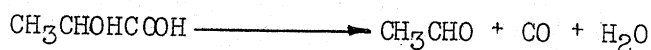
The dissociation of lactic acid in methanol has been reported by Mizutani (126).

Several papers not discussed herein are concerned with the Raman effect (31, 107), rotation dispersion (113), and infrared absorption (163) of lactic acid and its derivatives.

Thermal Decomposition

Lactic acid and related α -hydroxy acids (except acids, such as α -hydroxyisobutyric acid, that have a tertiary alcohol group) undergo auto-esterification readily when heated, forming both cyclic compounds (such as glycolide and lactide) and linear polymers (100). The linear polymer predominates under equilibrium conditions, whereas the cyclic dimer is formed in good yields when the partly esterified mixture is distilled under reduced pressures. Because of the ease with which α -hydroxy acids undergo auto-esterification, it seems likely that the thermal decomposition of α -hydroxy acids in their monomeric form has not been studied.

Regardless of the mechanism of the decomposition, however, the pyrolysis products reported for lactic acid and other aliphatic α -hydroxy acids are an aldehyde (or ketone), carbon monoxide, and water (100).

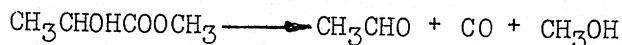
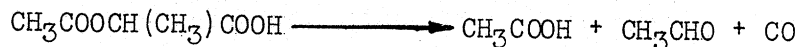


This general method has been used to convert α -hydroxylauric (42) and α -hydroxymyristic acids (115) into aldehydes that contain one less carbon atom.

Hurd (100) has suggested that the lactide is the intermediate that decomposes into aldehyde and carbon monoxide.

α -Hydroxyisobutyric acid, having a tertiary alcohol group, when heated, shows some tendency toward dehydration. For example, when this acid is distilled at atmospheric pressure, 30 percent of the lactide is produced, but about 15 percent is changed into methacrylic acid ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$) and about one-half into acetone (19).

The mono-esters of lactic acid when heated also decompose into aldehydes and carbon monoxide³.



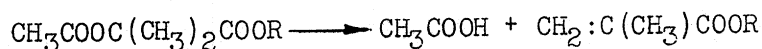
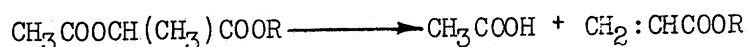
Under suitable conditions, the hydroxy esters undergo auto-alcoholysis (59). Ethyl lactate, for example, when heated in a closed vessel at 250° for 7 to 8 hours (59, 105), yields lactide and ethyl lactyllactate ($\text{CH}_3\text{CHOHCOOCH}(\text{CH}_3)\text{COOEt}$). It appears from an observation of Adkins and coworkers that certain

³ UNPUBLISHED RESULTS OF E. M. FILACHIONE AND COWORKERS.

β -hydroxy esters also are capable of entering into auto-alcoholysis (4).

The behavior of the di-esters of α -hydroxy acids on pyrolysis is largely a function of the alcohol radical. Esters of glycolic acid, which has a primary alcohol group but lacks β -hydrogen atoms, are relatively stable. Lactic esters derivatives of a secondary alcohol, are less stable. Esters of α -hydroxyisobutyric acid, being derived from a tertiary alcohol, are least stable.

Acrylic esters and acetic acid are obtained by the decomposition of alkyl- α -acetoxypropionates, whereas alkyl methacrylates are obtained from alkyl α -acetoxyisobutyrate.



Owing to another type of decomposition (caused by scission of the other ester group) olefines as well as the decomposition products of the acetoxy acid are formed in the pyrolysis of alkyl α -acetoxypropionates in which R is ethyl or a higher alkyl group. Table 5 shows the yields of acrylates as a function of R; also included is phenyl methacrylate (68).

Table 5. - Pyrolysis of Acetyl Lactic Esters $(\text{CH}_3\text{COOCH}(\text{CH}_3)\text{COOR})^a$

Acetyl lactic ester	Yield of acrylic ester, % ^b
Methyl	90
Ethyl	33
Benzyl	74
Tetrahydrofurfuryl	70-79
Allyl	43
Methallyl	41
beta-Methoxyethyl	31
beta-Ethoxyethyl	37
beta-Chloroethyl	51
iso-Butyl	40
Phenyl	80
o-Tolyl	75
p-Chlorophenyl	77
p-Cyclohexylphenyl	71
p-tert.-Butylphenyl	80
o-Allylphenyl	76.
Phenyl ^c	90

a. Vapors of the acetyl lactic ester were passed through a pyrex-glass tube heated at about 550° C. (33, 67, 152).

b. Based on the lactic ester decomposed.

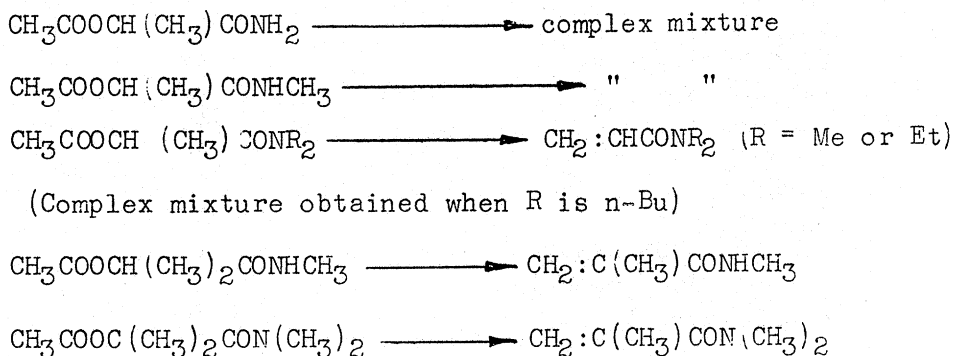
c. Phenyl acetoxyisobutyrate was transformed by pyrolysis into phenyl methacrylate.

As indicated by the pyrolysis behavior of the phenyl esters (Table 5), the α -hydroxyisobutyric acid derivatives decompose more readily than the corresponding lactates. In agreement with the relative thermal instability of the hydroxyisobutyrate is the behavior of ethyl α -ethoxyisobutyrate, which decomposes on distillation (about 155°) at atmospheric pressure, yielding ethyl methacrylate (18).

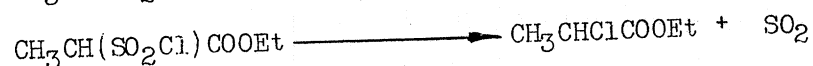
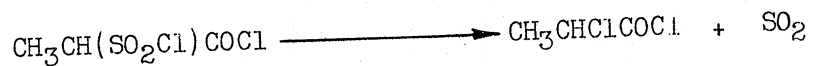
As has been shown in the preceding paragraphs, the decomposition behavior of the alkyl α -acetoxypropionates (and α -acetoxyisobutyrate) depends on the relative stability of the two ester groups in the molecule. The thermal decomposition of similar esters having three ester groups is of interest in this connection. The results outlined below show that certain ester groups differ greatly in thermal stability and that the course of the decomposition can be controlled moderately well by judicious selection of ester groups. (61, 66).

Acetate of	Corresponding unsaturated ester (principal product)
$\text{HOCH}(\text{CH}_3)\text{COOCH}_2\text{COOCH}_3$	$\text{CH}_2:\text{CHCOOCH}_2\text{COOCH}_3$
$\text{HOC}(\text{CH}_3)_2\text{COOCH}_2\text{COOCH}_3$	$\text{CH}_2:\text{C}(\text{CH}_3)\text{COOCH}_2\text{COOCH}_3$
$\text{HOC}(\text{CH}_3)_2\text{COOCH}(\text{CH}_3)\text{COOCH}_3$	$\text{CH}_2:\text{C}(\text{CH}_3)\text{COOCH}(\text{CH}_3)\text{COOCH}_3$
$\text{HOC}(\text{CH}_3)_2\text{COOCH}(\text{CH}_3)\text{COOCH}_2\text{CH}_3$	$\text{CH}_2:\text{C}(\text{CH}_3)\text{COOCH}(\text{CH}_3)\text{COOCH}_2\text{CH}_3$

The pyrolysis of the amides of α -hydroxy acids has received relatively little attention. It has been demonstrated, however, that (a) α -acetoxypropionamide yields a complex nature, (b) N,N-dimethyl- α -acetoxypropionamide yields N,N-dimethylacrylamide in high yield (the N,N-diethylacrylamide also is obtained in high yield by the pyrolysis of N,N-diethylacetoxypropionamide), and (c) certain N-alkylmethacrylamides can be obtained satisfactorily by pyrolysis of the corresponding α -acetoxyisobutyramides (144, 146):



Several investigators have pyrolyzed certain products obtained by treating lactic acid or lactic esters with thionyl chloride (20, 21, 41, 79, 78, 79, 80, 154). The decomposition of two of these products is outlined below:



These results show that the sulfinyl chloride group is unstable, decomposing before either the $-\text{COCl}$ or the $-\text{COOEt}$ groups.

The ether group of the triphenylmethyl ether of ethyl lactate also is less stable than the carethoxy group, the pyrolysis products being ethyl pyruvate (70% yield) and the triphenylmethane (101). The triphenylmethyl ether of ethyl lactate also is less stable than the acetyl group in methyl and ethyl acetyl lactates, which, on pyrolysis, yield acrylates (33, 152, 154).

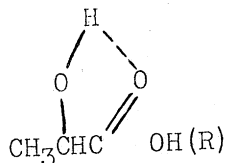
Reactions of the Hydroxyl Group

Before enumerating the various reactions in which the alcohol group of lactic acid participates, it is of interest to consider the extent to which this alcohol group would be expected to function as a typical alcohol.

Although lactic acid is a secondary alcohol, it does not have the two electron-releasing groups normally present in such alcohols. Since it has only one electron releasing group, the alcohol group in lactic acid might be expected to have some of the characteristics of a primary alcohol. Moreover, α -hydroxyisobutyric acid, a tertiary alcohol which resembles a secondary alcohol in having two electron-releasing groups, might be expected to behave partly as a secondary alcohol. The following facts indicate that lactic acid and α -hydroxyisobutyric acid, respectively, have some of the characteristics of primary and secondary alcohols (even though structurally they are secondary and tertiary alcohols).

1. Difficulty with which direct dehydration is achieved; it has not been established that lactic acid and lactic esters can be dehydrated directly.
2. Difficulty of transformation into halo acids by treatment with HCl or HBr .
3. Ease of acetylation with acetic anhydride.
4. Ease of acetylation with acetic acid (even α -hydroxyisobutyric acid, a tertiary alcohol, is esterified with acetic acid) (54).

Probably the behavior of the alcohol group in lactic acid and alkyl lactates is affected by hydrogen bonding with the carboxyl and carbalkoxy groups:



Since, according to Pauling (133, 134), this hydrogen bridge is weak, probably it has little effect on the reactivity of the alcohol group. Moreover, the common alcohols or alkanols are subject to hydrogen bonding, albeit intermolecular rather than intramolecular.

Lactic acid (or its esters or amides) undergoes many reactions characteristic of alcohols. Some of these "alcohol reactions" are:

1. Xanthation with carbon bisulfide (96, 97).
2. Esterification with acetic, lactic, and other organic acids (54, 62, 63, 125, 136).

Menschutkin compared the esterification reactivities of glycolic acid, lactic acid, and α -hydroxyisobutyric acid with (a) isobutyl alcohol, (b) acetic acid, and (c) auto-esterification (125). The resulting data on rate and equilibrium (Table 6) suggest that lactic acid is more easily acetylated with acetic acid than either glycolic or α -hydroxyisobutyric acid and show that the latter acid reacts with acetic acid even though it is a tertiary alcohol.

3. Alcoholysis (59, 105, 161).
4. Iodoform reaction (120).
5. Phosgene and lactic esters react, yielding chloroformates $\text{ROCOCH}(\text{CH}_3)\text{OCOCl}$ and carbonates (93, 154, 169).
6. Dehydrogenation yields pyruvic acid or its derivatives (91).
7. Oxidation under some conditions (oxygen in vapor phase) yields pyruvic acid or its derivatives (114).
8. Reaction of ethyl lactate with trichloroacetophenone in the presence of alkali alcoholate, yielding ethyl α -benzoyloxypropionate (98).
9. Reaction of ethyl lactate with cyanic acid (HOCN) (171):

$$2 \text{ CONH} + \text{HOCH}(\text{CH}_3)\text{COOEt} \longrightarrow \text{NH}_2\text{CONHCOOCH}(\text{CH}_3)\text{COOEt}$$
10. Acylation with various aliphatic and aromatic acid chlorides, including chloroformates (55, 149).
11. The alcohol group of lactic acid adds to one of the double bonds of di-cyclopentadiene, yielding an ether (27, 28, 29).
12. Diazomethane reacts with alkyl lactate, yielding the methyl ether (103).
13. Phenyl isocyanate reacts with ethyl α -hydroxybutyrate, yielding the urethane (9).

Table 6 - Relative Esterification Reactivities of Glycolic, Lactic and α -Hydroxyisobutyric Acids

Esterification	Rate	Equilibrium
Isobutyl alcohol with:		
Glycolic acid	-	67.67
Lactic acid	-	68.01
α -Hydroxyisobutyric acid	40.56	64.61
Acetic acid with:		
Glycolic acid	-	49.22
Lactic acid	-	56.48
α -Hydroxyisobutyric acid	2.49	12.06
Autoesterification:		
Glycolic acid	-	32.40
Lactic acid	-	32.16
α -Hydroxyisobutyric acid	2.61	10.83

14. α -Halo-acids react to give ethers. For example, the sodium derivative of ethyl lactate reacts with ethyl bromopropionate, yielding the ether ester (84, 85, 86, 102, 106).

It is of interest to compare the cleavage of ethers of lactic acid with a simple ether of a secondary alcohol. Thus, ethyl α -ethoxypropionate cleaved with hydrogen iodide results in the formation of ethyl iodide and lactic acid (34), whereas cleavage of ethyl isopropyl ether results in ethyl alcohol and isopropyl iodide.

15. The alcohol group of lactic acid reacts more readily than n-propanol with methyl sulfate, which might be taken as an indication that the hydroxyl group in lactic acid is more acidic than the hydroxyl group in n-propanol. The lactic acid hydroxyl group, however, is less readily methylated than materials such as phenol, benzyl alcohol, furfuryl alcohol, N-hydroxyethyl piperidine, mandelic acid, and 3-dimethylaminopropanol (26). Yields of methyl ether obtained under comparable conditions from the following compounds were (percent): Lactic acid, 15; benzyl alcohol, 64; 2-phenylethanol, 19; cinnamyl alcohol, 53; furfuryl alcohol, 70; propanol, 0; n-hydroxyethylpiperidine, 100; 3-dimethylaminopropanol, 100; and mandelic acid, 70.

16. Lactic acid derivatives are converted into inorganic esters by treatment with phosphorus oxychloride (80), thionyl chloride (20, 21, 41, 46, 70, 78, 79, 80, 127, 132, 154), and boric anhydride (170).

The reactivity of lactic acid toward the following alcohol reagents is slight; if there is a reaction, it produces abnormal products:

1. Hydrogen bromide gives 13 percent bromopropionic acid, and "very little chloropropionic acid is produced by the acid action of hydrogen chloride on lactic acid" (123).

2. Although the normal oxidation product (pyruvic acid) of a secondary alcohol can be obtained from lactic acid under certain conditions, the product ordinarily obtained with many oxidizing reagents is acetaldehyde (76).
3. Dehydration to acrylic acid or its derivatives does not occur under the usual dehydrating conditions; instead, acetaldehyde and carbon monoxide are formed (100).
4. According to Bruson (1), addition to the double bond of acrylonitrile does not occur.
5. Acetaldehyde instead of sulfates, ethers, and olefinic products, is formed in the presence of sulfuric acid (53, 58, 153).

Reactions of the Carboxyl Group

The carboxyl group in lactic acid differs from that in typical organic acids, such as acetic, in that the carbonyl group appears to be attached intramolecularly through a weak hydrogen bridge to the alcohol group, and lactic acid exists in the monomeric state, that is, it does not form dimers of the type found in acetic acid. Although the carboxyl group of lactic acid differs somewhat in structure from the carboxyl group of acetic and similar acids, the acid reactions of lactic acid appear to be normal. The hydroxyl group as well as the carboxyl group participates in some reactions (discussed in another section).

Salts. -- Many salts of lactic acid have been prepared, and some of them are made commercially (186, 187). No attempt will be made to discuss all of the reactions of lactic acid salts, but some of the reactions that lead to the formation of esters are:

1. Sodium d-lactate and ethyl p-toluenesulfonate give ethyl d-lactate in yields of more than 80 percent (108).
2. Benzyl chloride can be used similarly to prepare benzyl lactate in approximately 55 percent yields (87).
3. Potassium lactate and ethyl chloropropionate yield ethyl lactyllactate. (184).
4. Direct esterification of ammonium lactate with butanol yields butyl lactate, ammonia and water (60).

The salts of lactic acid appear to be less suitable for conversion into esters, via reaction with alkyl halides, than the salts of acids such as acetic and other relatively weak acids.

Reaction of lactic acid with o-phenylene diamine, which gives a benzimidazole, has been used as the basis of an analytical method (50, 162).

Esterification -- Lactic acid undergoes esterification readily with various alcohols, and many lactic esters have been described in the literature. The reported yields, however, are frequently low. Probably the low yields of lactic esters have been due largely to the fact that the esterification is complicated by the formation of auto-esterification products such as polylactic acid and alkyl polylactates. Moreover, some of the available grades

of lactic acid are impure aqueous solutions, and hence are less easily esterified. In more recent investigations, conditions have been found under which lactic esters can be obtained in high yields (56, 61, 64, 66, 147, 152).

Many high-boiling esters of lactic acid have been prepared (56, 59, 68, 148, 149), and evaluated as plasticizers (59, 68, 148) for vinyl chloride resins. For the esters within a homologous series, relations were found between molecular weight (or carbon atoms) and the physical constants, that is, boiling point, vapor pressure, density, refractive index and viscosity (149, 150).

Reactions of the Ester Group in Alkyl Lactates

The ester group of alkyl lactates appears to behave normally in the usual ester reactions, although there is reason to believe that the factors (43) responsible for the relatively high dissociation constant of lactic acid influence also the properties of lactic esters.

Hydrogenation (2, 3, 24) or reduction with sodium (118) transforms alkyl lactates into propanediol 1,2.

D'Ianni and Adkins (48) found that hydrogenation of N-pentamethylenelactamide (nitrogen analog of a lactic ester prepared by the interaction of ethyl lactate and piperidine) gives 51 percent 1-piperidino-2-propanol; 10 percent, 1,2-dipiperidinopropane; 10 percent 1,2-propanediol; 10 percent piperidine; and 4 percent N-n-propylpiperidine. Clemmensen and Heitman (37) reported that ethyl lactate and urea react in the presence of strong alkaline catalyst, yielding the hydroxydiureide, $(\text{CH}_3\text{CHOHCONH})_2\text{CO}$. However, Stoughton (166) has shown that the product of this reaction is 5-methyl-2,4-oxazolidinedione.

Hammett and Pfluger (89,90) investigated the methylation of trimethylamine



with the methyl esters of various acids, and observed that the methylating effect of the ester was related to ionization constants of the corresponding acids. A linear relation was found between the methylation rate constants, and the ionization constants of the acids; some of their data are given in Table 7.

Table 7. - Methylation of Trimethylamine with RCOOCH_3^a

Methyl ester	Alkylation constant	Ionization constant (25°)	Hydrolysis constant
Acetate	0.00593	0.0000186	100
Benzoate	.0161	.000068	25.9
o-Toluate	.0166	.000135	-
p-Toluate	.0123	.000044	12.1
o-Chlorobenzoate	.0727	.00132	49.5
Phthalate	.1243	.000654	-
o-Nitrobenzoate	.33	.0065	148
Lactate	.0351	.000138	968

a. Hammett and Pfluger, (90).

Hydrolysis of Lactic Esters. -- Salmi (156, 157) has published data on the velocity of hydrolysis of methyl esters of lactic and other hydroxy acids (Table 8). It was shown that methyl glycolate and methyl lactate hydrolyze more rapidly than the corresponding aliphatic esters, whereas the higher α -hydroxy esters (butyric, valeric, caproic and heptanoic) hydrolyze somewhat more slowly than the corresponding normal aliphatic esters. The α -methoxy esters and unsaturated esters had relatively high and low hydrolysis rates, respectively.

Table 8. - Hydrolysis Constants at 25°C. of Methyl Esters
(in 0.208 N HCl)^a

Methyl ester	Constant	Methyl ester	Constant
Butyric	0.00423	α -Hydroxycaproic	0.00405
Valeric	.00441	α - " heptanoic	.00391
Caproic	.00410	Propionylformic	.00300
Heptanoic	.00412	Butyrylformic	.00296
Isovaleric	.00151	α -Methoxybutyric	.000743
Methylethylacetic	.00138	α -Methoxyvaleric	.000741
Trimethylacetic	.000709	α -Methoxycaproic	.000776
Glycolic	.00716	Acrylic	.000282
Lactic	.00780	Vinylacetic	.00423
α -Hydroxybutyric	.00391	Allylacetic	.00345
α -Hydroxyvaleric	.00398	delta-Hexenoic	.00346

a. Salmi (156).

Williams, Gabriel, and Andrews (181) determined the hydrolysis equilibrium constants of the ethyl esters of several acids, including lactic acid, and concluded that esters of relatively strong acids are more completely hydrolyzed under comparable conditions than esters of weaker acids. Table 9 gives some of their data.

Table 9. - Hydrolysis Equilibrium Constants of Ethyl Esters^a

Ethyl ester	K_E	$K_A \times 10^{-5}$
Acetic	0.296	1.8
Propionic	.289	1.34
Glycolic	.44	15.2
Lactic	.38	14.0

a. Williams, Gabriel, and Andrews (181).

Dietz, Degering and Schopmeyer (49) determined the equilibrium constant for the ethyl lactate esterification both by hydrolysis of ethyl lactate and by esterification of lactic acid. Their value for K under refluxing conditions is 2.71 ± 0.06 .

Berger (14) studied the hydrolysis of several ethyl esters under both neutral and acidic conditions. His results (Table 10) indicate that the rate of hydrolysis is roughly directly proportional to the strength of the corresponding acid, whereas the effect of the catalyst is inversely proportional to the strength of the corresponding acid.

Table 10. - Hydrolysis of Ethyl Esters at 40.5° C.^a

Ethyl ester	K (catalyzed)	Q ^b	A ^c
Trichloroacetic	4.65	2.2	121
Dichloroacetic	1.96	15	5.1
Chloroacetic	1.51	32	.155
Lactic	1.55	1700	.0138
Acetic	1.05	2600	.0018
Butyric	.83	4700	.0015
Isobutyric	.88	8750	.0014
Propionic	.93	22000	.0013

a. Berger (14).

b. Ratio of catalyzed to noncatalyzed hydrolysis.

c. Affinity constant

Colon and Warner (39) observed that the rate of alkaline hydrolysis of n-alkyl lactates decreases as the size of the alkyl group increases, the most pronounced difference in rate being between methyl and ethyl. The rate of acid hydrolysis was virtually independent of the alkyl group. Table 11 gives some of the data of these investigators.

Some of the data of Salmi and Leino (Table 12) illustrate the effects of both the acid and alcohol components on the alkaline hydrolysis of glycolic, lactic, and α -hydroxyisobutyric esters (158). The corresponding glycolic and lactic esters hydrolyzed at about the same rates, although the rates for the glycolic ester were slightly higher than those for the lactic esters, indicating that the presence of one methyl group on the α -carbon has little effect on the hydrolysis rate. The hydrolysis of the hydroxyisobutyric esters, however, was much slower than that of the glycolic and lactic esters, showing that the location of a second methyl group on the α -carbon greatly retards the hydrolysis. In agreement with the work of Colon and Warner (39), the methyl esters hydrolyzed much more rapidly than the ethyl, propyl and butyl esters. The isopropyl ester was most resistant to hydrolysis. The allyl esters hydrolyzed much more rapidly than the n-propyl esters. Esters made from alcohols having negative groups on the β -carbon hydrolyzed more rapidly than those having the negative groups further removed from the ester group.

Table 11. - Hydrolysis of Lactic Esters

Lactic ester	k (liters mole ⁻¹ min. ⁻¹)		Activation energies, cal.
	0° C.	15° C.	
Methyl ^a	21.3	59.2	10,600
Ethyl ^a	8.98	24.1	10,300
n-Propyl ^a	7.06	19.4	10,500
n-Butyl ^a	6.79	19.0	10,700
(Ethyl acetate) ^a	1.17	3.16	10,400
(Ethyl propionate) ^a	1.14	3.00	10,200
	30° C.	40° C.	
Methyl ^b	9.48	20.1	14,100
Ethyl ^b	10.00	20.7	13,700
n-Propyl ^b	9.73	20.4	13,900
n-Butyl ^b	8.70	18.3	14,000
	40° C.	60° C.	
Methyl ^c	25.9	118	15,700
Ethyl ^c	23.8	113	16,200
n-Propyl ^c	22.7	111	16,500

a. Alkaline

b. Acid

c. In the absence of catalyst

Table 12. - Alkaline Hydrolysis of Glycolic, Lactic, and α -Hydroxyisobutyric Esters at 25°, ^a, ^b

Alcohol group	Glycolic ester, k_{25}^{25}	Lactic ester, k_{25}^{25}	Hydroxyisobutyric ester, k_{25}^{25}
Methyl	115.1	109.3	24.9
Ethyl	60.5	54.5	7.76
n-Propyl	55.2	46.1	6.13
n-Butyl	50.7	41.1	5.19
iso-Propyl	13.1	12.3	1.26
2-Methoxyethyl	143.0	125.1	28.2
2-Ethoxyethyl	145.5	124.0	29.6
2-Propoxyethyl	127.4	-	-
3-Methoxypropyl	76.6	68.3	15.9
4-Methoxybutyl	-	61.8	-
2-Chloroethyl	186.4	178.1	46.0
3-Chloropropyl	100.2	99.1	19.5
Allyl	112.7	104.8	23.1

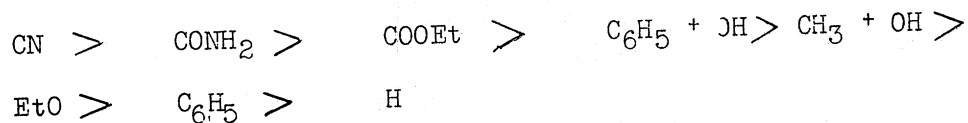
^a: Salmi and Leino (158).^b: 0.009 N NaOH was used.

Krige and Hollow (112) studied the alkaline hydrolysis of ethyl lactate, giving 1.82 as the temperature coefficient and 10,500 cal. as the energy of activation.

Alcoholysis of Lactic Esters. --- Lactic esters (33, 56, 65, 152) and lactide (35, 36) undergo alcoholysis readily with various primary and secondary alcohols. It is interesting that alcoholysis of lactide in which only a trace of catalyst is used produces esters of lactic acid (35, 36). Tertiary alcohols react only slowly with alkyl lactates, but tert.-butyl lactate has been prepared by the interaction of tert.-butanol and lactide³.

Ammonolysis and Aminolysis of Lactic Esters. -- In agreement with the generalization that the reactivities of esters toward ammonia parallel their ease of alkaline hydrolysis, lactic esters undergo amide formation more readily than those of the unsubstituted aliphatic acids (57). For example, 30- to 50-percent yields of lactamide were obtained when the methyl, ethyl, propyl, and butyl esters of lactic acid were allowed to stand with liquid ammonia at room temperature (82,110), whereas butyl acetate, ethyl benzoate, methyl salicylate, and glyceryl monoacetate were substantially unreactive under similar conditions.

The effect of substituents in the alpha position of ethyl acetate has been determined (10); the α -substituted esters in decreasing order of reactivity are:



These results show that hydroxyl groups, as well as other electron-attracting groups in the alpha position enhances the reactivity of an ester toward ammonia (30,57). Other α -substituted esters relatively reactive in ammonolysis and aminolysis reactions are: Monochloroacetic, dichloroacetic, trichloroacetic, dibromoacetic, chloropropionic, and oxalic esters (57).

Since ethyl isobutyrate reacts slowly with ammonia, and no reaction is observed with ethyl trimethylacetate, it appears that electron-releasing groups on the α -carbon decrease reactivity of an ester toward ammonia and amines (45, 177). Electron-releasing groups in the alcohol radical of esters also decrease reactivity toward ammonia (72). It is also known that tert.-butylamine is less reactive than n-butylamine (25).

Ratchford (143, 144, 146) prepared many N-substituted lactamides by aminolysis of methyl lactate and collected much information on the relation between the structure of the amine and its reactivity toward methyl lactate. Primary n-alkyl amines (even those having molecular weights as high as that of n-octadecylamine) reacted readily and almost quantitatively with methyl lactate at about room temperature. Aniline, possibly because it is a weak base, reacted less readily. Cyclohexylamine reacted with lactic esters (81). Dimethylamine reacted readily, giving a high yield of N,N-dimethyl lactamide, but diethylamine and the higher di-alkylamines were unreactive. Cyclic secondary amines, such as morpholine and piperidine, however, gave high yields of the corresponding lactamide. Diethanolamine, a substituted secondary amine, also reacted readily with methyl lactate.

Other observations made by Ratchford (144, 146) are of interest in connection with the reactivity of lactic and other esters toward amines. Methyl α -hydroxyisobutyrate, which has two electron-releasing groups attached to the α -carbon, reacted readily with methylamine but failed to react with dimethylamine.

Although methyl lactate failed to react with diethylamine, polylactic acid (a lactate of an alcohol, $\text{HOCH}(\text{CH}_3)\text{COOR}$, having an electron-attracting group on the β -carbon atom) reacted slowly, yielding the desired N,N-diethyl lactamide (144, 146). These and other available data indicate that negative substituents near the ester group (in either the acid or the alcohol component of the ester) increase reactivity toward primary and secondary amines.

Gordon, Miller and Day (44, 88) have made a careful study of the ammonolysis of various alkyl lactates and of many other esters. Some of their results are given in Tables 13 and 14.

Reporting further results in this field, Day (44, 88) described the mechanism of the ammonolysis and pointed out that polyhydric alcohols increased the rate greatly. The role of the amine was studied also. The following relative rates of aminolysis of methyl acetate illustrates the effect of amine structure: Methylamine, 100; ethylamine, 13; n-propylamine, 10.3; ammonia, 1.6; isopropylamine, 0.495; and t-butylamine, very slow.

Table 13. - Relative Reaction Rates for Ammonolysis of Lactic Acid Esters at 30° C.

Lactic ester	30 hr.	50 hr.
Methyl	1.00	1.00
Allyl	.997	-
Ethyl	.262	.221
n-Propyl	.204	.197
n-Butyl	.204	.197
n-Amyl	.139	.139
iso-Butyl	.136	.134
iso-Propyl	.0667	.0521
sec.-Butyl	.0551	.0509
(n-Butyl hydracrylate ^a)	.0461	.0398
tert.-Butyl	.0116	.0111

a. Tabulated for comparison with n-butyl lactate.

Table 14. - Relative Reaction Rates for Ammonolysis of Methyl Esters at 25° C.

Methyl ester	50 hr.	100 hr.	200 hr.
Formate	308 ^a	321 ^a	367 ^a
Lactate	7.2	7.5	7.9
Acetate	1.00	1.00	1.00
Phenylacetate	.938	.906	.893
Crotonate ^b	.580	.692	.881
Propionate	.564	.485	.412
Benzoate	.376	.239	.138
Isobutyrate	.176	.151	.119
Trimethylacetate	.00294 ^c	.00306 ^c	.0033 ^c

a. Calculated from data obtained in a period less than that specified.

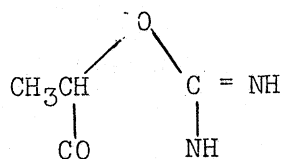
b. Principal reaction was 1,4-addition.

c. Taken from Data for 388 hrs.

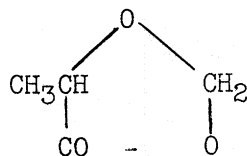
Reactions of Both the Hydroxyl and Carboxyl Groups

Some reagents react with both functional groups in lactic acid, alkyl lactates, and lactamides. Frequently ring compounds are obtained in these reactions. Several reactions of this type are:

1. Ketene reacts with lactic acid, yielding α -acetoxypropionic anhydride (77, 83).
2. Lactic acid, when allowed to react with methyl acetate, yields methyl lactate and methyl α -acetoxypropionate (140, 151).
3. Alkyl lactates react with urea, forming 5-methyl-2,4-oxazolidine diones (8, 166).
4. Ethyl lactate reacts with guanidine (172), the product being 4-oxo-2-imino-5-methyl oxazolidine:



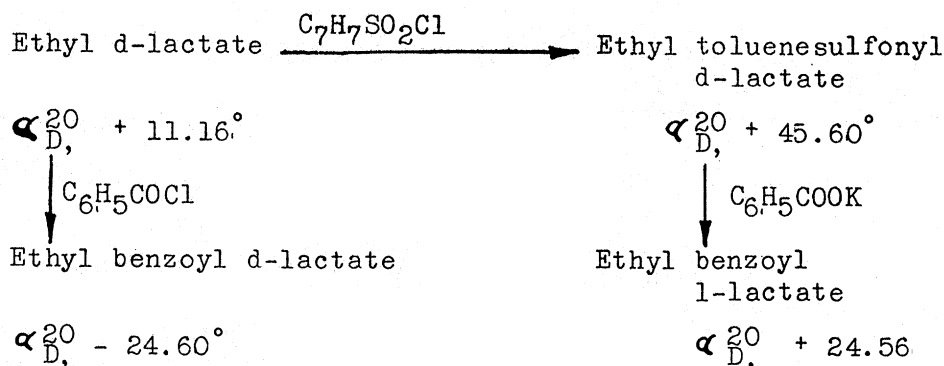
5. Lactamide and methyl carbonate react, yielding an oxazolidinedione, 5-methyl-2,4-dioxo-oxazolidine (173).
6. Cyclic compounds are formed when aldehydes and ketones react with lactic acid (or with lactamide), the structure of the formaldehyde-lactic acid product (95) being



The formaldehyde product boils at 153-4° C. (95). Similar products (182) are formed from acetaldehyde (131), propionaldehyde (131), isobutyraldehyde (131), and acetone (130). The reaction of lactic acid (22, 94, 124, 159) and ethyl lactate (69) with chloral has been studied by several workers; the product from lactic acid and chloral is analogous to the formaldehyde product shown above; the ethyl lactate product was described as having the following structure (69): $\text{CCl}_3\text{CH}(\text{OH})\text{OCH}(\text{CH}_3)\text{COOEt}$.

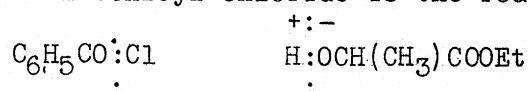
Toluenesulfonates as Intermediates in the Preparation of Lactic Acid Derivatives

The toluenesulfonate of lactic acid and alkyl lactates is of considerable interest because (a) it can be used conveniently to prepare many lactic acid derivatives, and (b) the transformation of the toluenesulfonate into other compounds is accompanied by inversion. The phenomenon of inversion can be used, for example, to convert d-lactic acid into an l-lactic acid derivative (108):

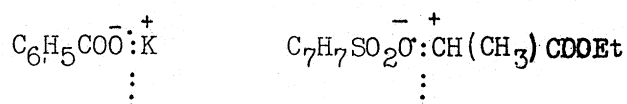


Whether or not inversion occurs in the reactions outlined above seems to depend on which bonds are polarized and cleaved. The probable polarizations and positions of cleavage are indicated below:

When benzoyl chloride is the reactant (no inversion).



When potassium benzoate is the reactant (complete inversion):



To illustrate the importance of the toluenesulfonates as useful chemical intermediates, several reactions of the toluenesulfonate of ethyl lactate are listed in Table 15. (108).

Table 15. - Reactions of the p-Toluenesulfonate of Ethyl Lactate

Reagent	Product	Yield, percent
Lithium chloride	-Chloropropionate	87
Sodium bromide	-Bromopropionate	94
Potassium iodide	-Iodopropionate	100
EtOMgI	- "	60
EtMgBr	-Bromopropionate	
PhMgBr ^a	- "	
NaOEt	-Ethoxypropionate ^b	
K ₂ CO ₃ +EtOH	- "	
NaOC ₆ H ₅	-Phenoxypropionate	
CH ₃ COOK	-Acetoxypropionate	80
C ₆ H ₅ COOK	-Benzoyloxypropionate	approx. 99
Ph ₄ OH	Toluenesulfonyloxypropionamide	
C ₆ H ₅ CH ₂ COOK	-Phenylacetate	

a. Ethylbenzene is formed from PhMgBr and ethyl toluenesulfonate.

b. Prepared also from the interaction of ethyl toluenesulfonate and the sodium derivative of ethyl lactate (108).

When treated with ammonia, the toluenesulfonate of ethyl lactate yields the amide of alanine ($\text{CH}_3\text{CHNH}_2\text{CONH}_2$) (74).

The toluenesulfonyl derivative of other lactic acid derivatives has been used as an intermediate in similar transformations (13). Some of these are given in Table 16.

Table 16. - Reactions of p-Toluenesulfonates of Lactic Acid Derivatives^a

Toluenesulfonate of	Reagent	Product (α -substitued)
Lactyl chloride	Lithium chloride	Chloropropionyl chloride
Lactamide	Potassium acetate	Acetoxypropionamide
"	Potassium benzoate	Benzoyloxypropionamide
Lactanilide	Potassium acetate	Acetoxypropionanilide
"	Potassium benzoate	Benzoyloxypropionanilide
Ammonium lactate	Potassium acetate	Acetoxypropionic acid
Lactyl derivative of anthranilic acid	Lithium chloride	Chloropropionyl derivative of anthranilic acid

- a. The toluenesulfonyloxypropionyl derivative of sodium p-aminobenzoate reacted with itself (polymerized), yielding the polymer having the segment

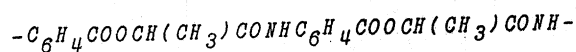


FIG. 1. COMPOSITION OF AQUEOUS LACTIC ACID SOLUTIONS
AND DEHYDRATED LACTIC ACID.

DATA FROM BEZZI (15) AND WATSON (174)

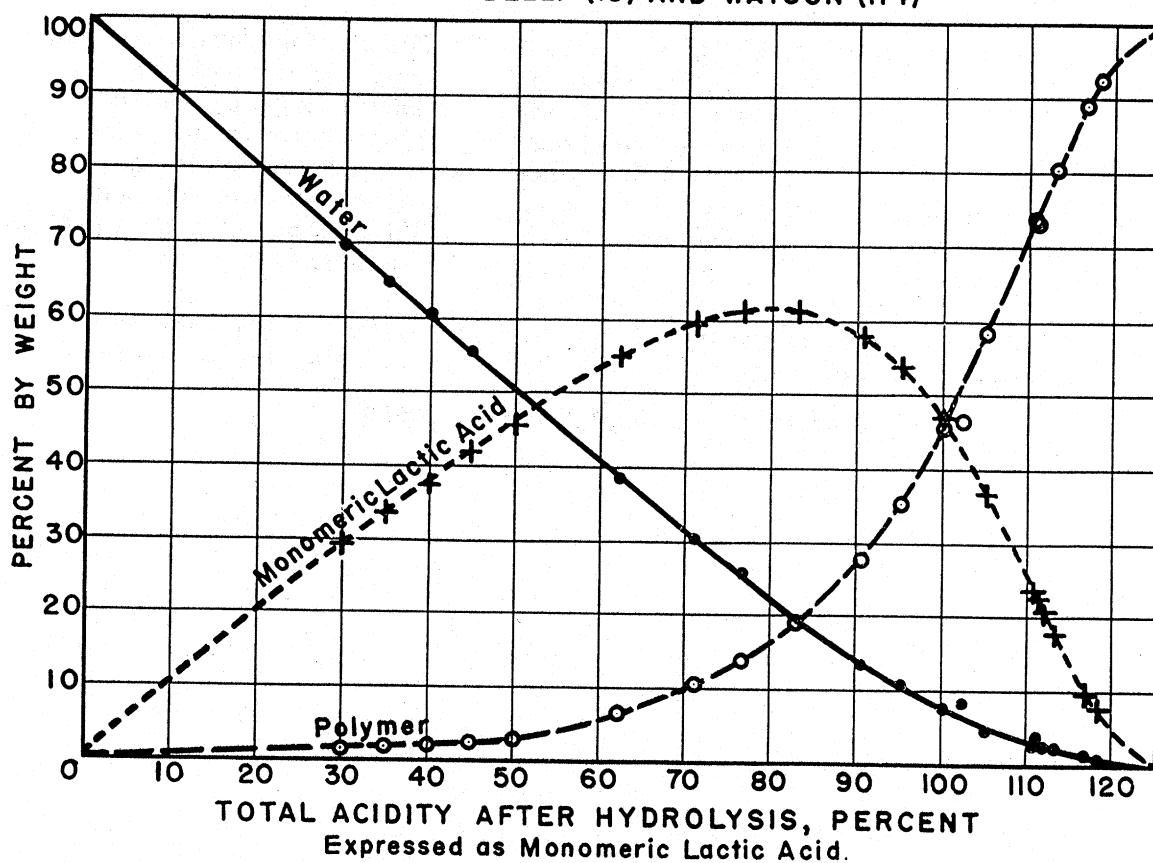


FIGURE 2. BOILING POINTS OF LACTIC AND RELATED HYDROXY ACIDS.

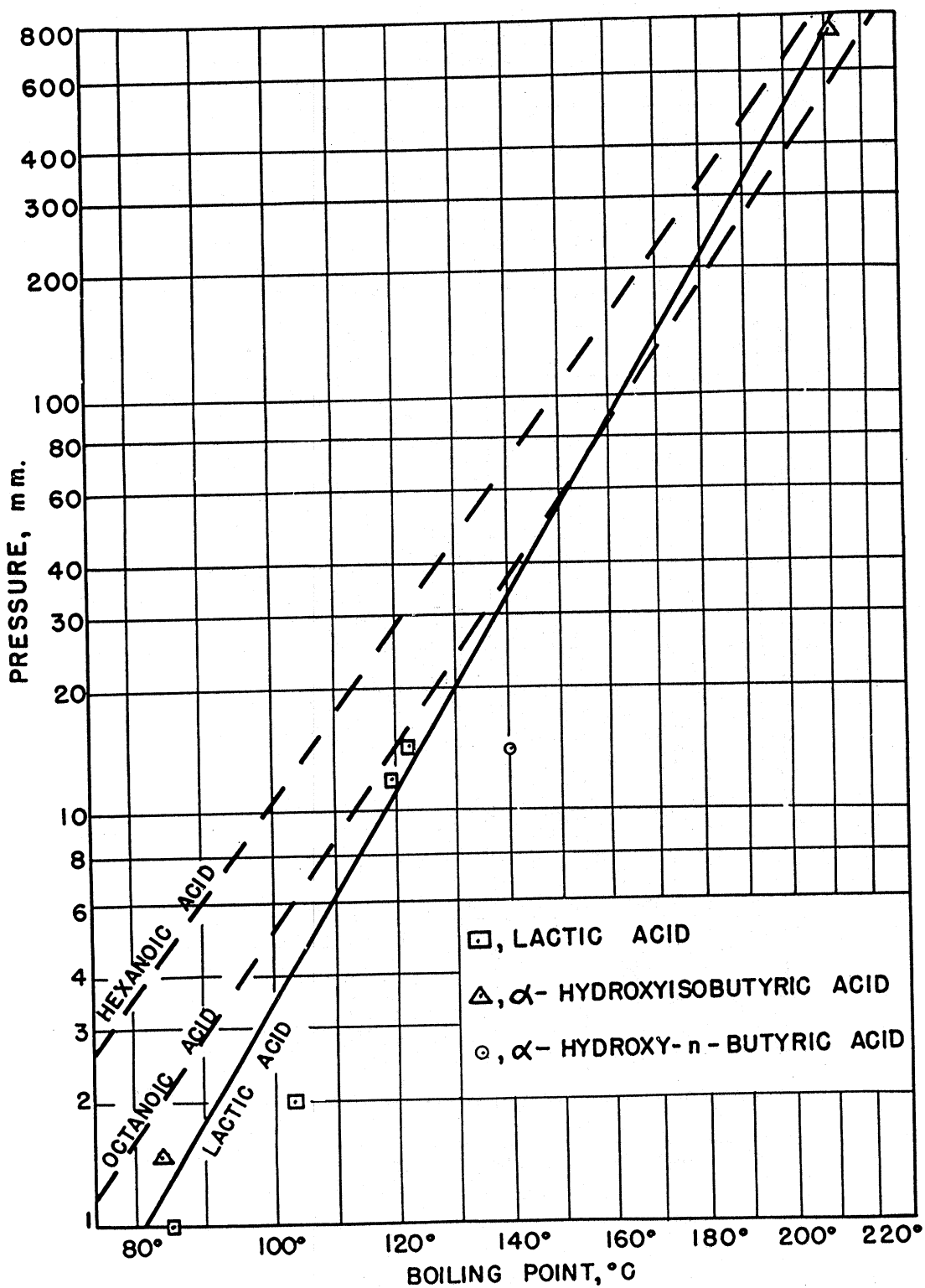
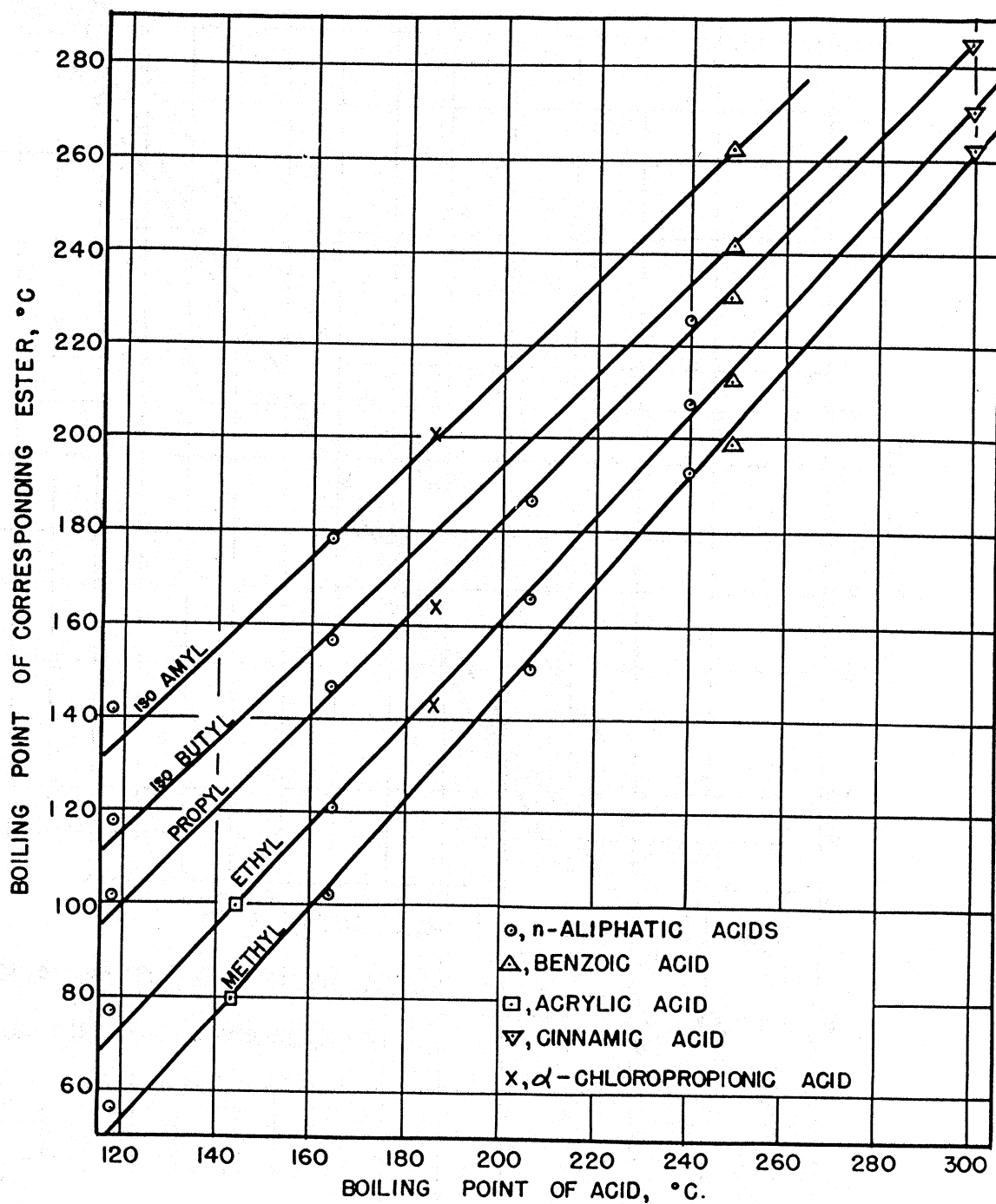


FIGURE 3. RELATION BETWEEN NORMAL BOILING POINTS OF ACIDS AND THEIR ESTERS.



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